



The transfer behavior of different ions across anion and cation exchange membranes under vanadium flow battery medium

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HIGHLIGHTS

- The transfer behavior of different ions across membrane was investigated in VFB.
- VX-20 and Nafion 115 were selected to investigate the transfer behavior.
- The capacity fade mechanisms of different membranes were investigated.

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ABSTRACT

The transfer behavior of different ions (V^{2+} , V^{3+} , VO^{2+} , VO_2^+ , H^+ , SO_4^{2-}) across ion exchange membranes is investigated under vanadium flow battery (VFB) operating condition. VX-20 anion exchange membrane (AEM) and Nafion 115 cation exchange membrane (CEM) are selected to investigate the influence of fixed charged groups on the transfer behavior of different ions. The interaction between different ions and water is discussed in detail aiming to ascertain the variation of different ions in the charge–discharge process. Under the VFB medium, the transfer behavior and function of different ions are very different for the AEM and CEM. V^{2+} ions at the negative side accumulate when VFB is assembled with Nafion 115, while the VO_2^+ ions at the positive side accumulate for VX-20. The SO_4^{2-} ions will transfer across Nafion 115 to balance the charges and the protons can balance the charges of VX-20. Finally the capacity fade mechanism of different membranes is investigated, showing that the capacity decay of VFB assembled with Nafion 115 mainly results from the cross mix of vanadium ions across the membrane, however, for VX-20, the side reactions can be the major reason. This paper provides important information about electrolyte for the application of VFB.

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1. Introduction

Renewable energy sources such as solar and wind power have attracted global attention, due to the current critical issues of energy shortage and air pollution. [1–3] However, these unstable and discontinuous renewable energies need to be combined with large-scale energy storage to improve their stability and to realize their stable output. Thus, large-scale energy storage becomes the key technology that realizes the wide application of renewable energies. [1,4].

The vanadium flow battery (VFB), which is firstly proposed by Maria Skyllas-Kazacos and co-workers in 1985 [5,6], has been

regarded as one of the most competitive candidates for the large-scale energy storage [7], owing to its high energy efficiency, long cycle life, high safety and environmentally friendly, etc. [8–12].

In a VFB, the power rate and energy can be designed independently. Its power rate is determined by the electrode area and the number of the VFB single cells, while, its energy can be controlled by the volume and concentration of vanadium electrolytes. The transfer behavior of electrolytes plays an significant role in determining the VFB performance, especially the capacity decay. For example, the diffusion of vanadium ions across the membrane will lead to the self-discharge and side reactions at the positive and negative sides, which further affects the VFB capacity over long-term charge–discharge cycling. [12,13] Maria Skyllas-Kazacos and co-workers investigated the water transfer behavior across CEMs and found that the direction of preferential water transfer is dependent on the state of charge (SOC) of the vanadium

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electrolytes. [14] Later on, transfer behavior of different vanadium ions across the membranes during charge and discharge was investigated as well. Concentration profiles of the different vanadium ions have been modeled in order to predict expected capacity loss over extended charge–discharge cycling. [15] However, the VFB medium is very complex [7], different ions like vanadium ions, sulfates ions and protons coexisted in the electrolyte, the interaction between them and water is obscure so far. At the same time, the state of vanadium electrolyte and the transfer behavior of different ions are closely related to the ion exchange membranes, the characteristics of membranes, e.g. the functional charged groups, the backbone, the micro structures, will greatly affect their transfer behavior. [8,16,17] However, the current research is mostly related perflourinate CEMs [14], seldom research was focused on AEMs. In addition, an overwhelming majority of the researches about vanadium electrolyte was accomplished under the atmosphere with the protection of inert gas like nitrogen or argon [18], even though, the V^{2+} ions can be easily oxidized even at very low concentration of oxygen [19], which makes the results more confusing. In this article, the glove box with 99.999% argon and less than 1 ppm oxygen is used to eliminate the influence of oxygen.

To understand the change of different ions in the charge–discharge process, two kinds of membranes with different ion exchange groups (Nafion 115 CEM and VX-20 AEM) were selected to investigate the transfer behavior and of different ions across them in detail. The changes of different ions in electrolyte were detected during charge–discharge process, and the transfer behavior of different ions was thoroughly discussed as well. The article fully investigated the different ions change phenomena in VFBs sandwiched with Nafion 115 and VX-20, respectively. Moreover, the primary reason of the capacity decay of VFB assembled with Nafion 115 or VX-20 as membrane was investigated.

2. Experimental section

All experiments described below were done in the glove box with 99.999% argon and less than 1 ppm oxygen. All experiments described below were done at 25 °C and under the standard atmospheric pressure. All the measurements were based on at least three samples, and the average values were used. The standard deviation on the measurements is about 5%.

A VFB single cell was employed to investigate the transfer behavior of water, vanadium ions, sulfate ions and protons during charge–discharge. The VFB cell was assembled with a membrane between two carbon felt electrodes, clamped by two graphite polar plates. The active area of electrode was 48 cm². Nafion 115 (DuPont company, CEM) and VX-20 (Fumatech company, AEM) were selected as ion exchange membranes. The original volume of the electrolytes at each side was 100 mL containing 1.7 M VO^{2+} in positive electrolyte and 1.7 M V^{3+} in negative electrolyte. The volume of positive and negative electrolytes at the end of discharge process was recorded during operation of the VFB. A 2 mL sample was collected from the positive and negative electrolyte, respectively, at the end of a discharge process in a different cycle for further analysis. The charge–discharge performance of the VFB was conducted by using a charge–discharge controller (Model BT 2000, Arbin Instruments Corp., USA). The upper limit voltage of charge was 1.55 V, the lower limit voltage of discharge was 1.0 V. The current density was kept at 80 mA cm⁻².

The concentration of vanadium ions with different valences was measured via auto potentiometric titrator (Mettler Toledo, T50) by using standard potassium permanganate solution as titrant. The concentration of sulfate ions was measured by method of precipitation, the barium chloride solution was used as precipitant. The

concentration of protons was measured by acid-base titration and standard sodium hydrate solution as titrant.

The permeability of vanadium ions was detected using a diffusion cell, as described earlier. [20] The diffusion cells were separated by a membrane. The left cell was filled with 1.7 M vanadium ions with different valences in 3 M H₂SO₄ solution, while the right one was filled with the mixture of MgSO₄ and H₂SO₄ in order to equalize the ionic strengths and to minimize the osmotic pressure effects before the test of vanadium permeability. Both sides were vigorously stirred by magnetic stirrers to avoid concentration polarization. Samples from the right cell were collected at regular time interval. The concentration of vanadium ions was characterized by using auto potentiometric titrator and UV–Vis spectrometer.

3. Results and discussion

3.1. The transformation of the water in electrolyte

To investigate the water transformation across the different kinds of membranes, the electrolyte volume was recorded at the end of a discharge process in a different cycle. Fig. 1 shows the change of electrolyte volume in the positive and negative half-cells when using Nafion 115 and VX-20 as membranes respectively. For Nafion 115, the electrolyte volume increases at the positive side and decreases at the negative side as cycle proceeding. The electrolyte transfers obviously during the first 10 cycles, then, the electrolyte volume hardly changed. However, for VX-20 AEM, the volume of electrolyte at positive side first increases then decreases during the cycle test, and the changing tendency is opposite at the negative side, indicating the transfer direction of water changed from “negative-to-positive” to “positive-to-negative” during the operation of the VFB. This phenomenon is possibly closely related to the transfer behavior of protons, which will be discussed later.

3.2. The transformation of vanadium ions in electrolyte

The vanadium ions normally could transfer through the ion exchange membranes during the operation of a VFB. [13] To investigate the change of vanadium ions in the electrolyte during the VFB operation, the samples were withdrawn from the positive and negative electrolyte at the end of a discharge process in different cycles and the concentration of vanadium ions with different valences was detected.

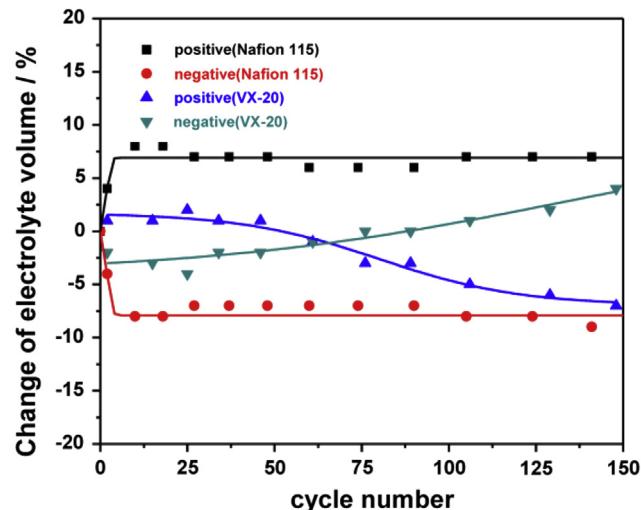
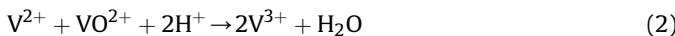
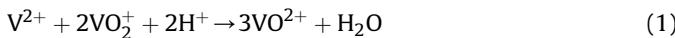


Fig. 1. Change of electrolyte volume in the positive and negative half-cells during cycle process when using Nafion 115 or VX-20 as membrane.

Fig. 2a displays the amount of vanadium ions in the positive and negative electrolyte when using Nafion 115 as membrane at the end of discharge process. The amount of VO^{2+} increases and the amount of VO_2^+ scarcely changes at the positive side, however, the amount of V^{2+} increases and the amount of V^{3+} decreases at the negative side after discharge process. The amount of V^{2+} at the negative side and VO_2^+ at the positive side mismatch after discharge, and the tendency becomes more clear as cycles proceeding. This phenomenon maybe caused by the transfer behavior of vanadium ions. Due to the diffusion coefficient of V^{2+} across Nafion 115 is the highest among the vanadium ions with different valences [21], more V^{2+} ions will transfer to positive side during charge–discharge process and react with VO^{2+} or VO_2^+ at the positive side (self-discharge reactions), according to the following reactions:

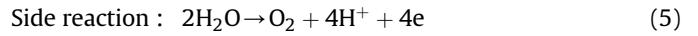
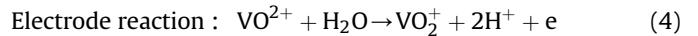


Due to the high diffusion rate of V^{2+} across Nafion 115, more VO_2^+ will be reduced by V^{2+} at the positive side during charge process. For example, if 1 mol V^{2+} ions diffuse from negative to positive side, 2 mol VO_2^+ ions will be reduced by V^{2+} according to Eq. (1). The amount of VO_2^+ at the positive side is less than that of V^{2+} at the negative side. To reach the upper limit voltage of charge, more V^{2+} will generate at the negative side at the end of charge process. Vanadium ions transfer across membrane continuously during charge and discharge process. During discharge process, more VO_2^+ will be reduced by V^{2+} at the positive side as well according to Eq. (1). When reach the lower limit voltage of discharge, part of V^{2+} will surplus in

the negative and VO_2^+ will be consumed in the positive at the end of discharge process. As a result, the V^{2+} ions will be accumulated with cycle proceeding. Meanwhile, V^{3+} amount will decrease at the negative side due to the transfer of vanadium ions and the accumulation of V^{2+} . From Eq. (1), VO_2^+ is consumed by V^{2+} and the generated V^{3+} will be oxidized to VO^{2+} by VO_2^+ immediately at the positive side (Eq. (3)). So the amount of VO^{2+} increases after discharge process according to Eqs. (1) and (3). The amount of total vanadium ions in the positive and negative electrolyte after discharge process shown in **Fig. 2b**. The amount of vanadium ions increases in the positive electrolyte ($\text{VO}^{2+}, \text{VO}_2^+$) and decreases in the negative electrolyte ($\text{V}^{2+}, \text{V}^{3+}$) as cycling, which coincides with the previous reported results. [18] The net transfer direction of vanadium ions is from negative to positive side due to different diffusion coefficients of vanadium ions with different valences [21].

Fig. 2c illustrates the amount of different vanadium ions in the positive and negative electrolyte using VX-20 as membrane at the end of discharge process. The amount of VO^{2+} decreases and the amount of VO_2^+ increases within a very narrow range in the positive electrolyte, while the amounts of V^{2+} and V^{3+} almost unchanged in the negative electrolyte respectively. As we know, the electrode reactions maybe accompany with the side reactions during charge process:

Positive:



Negative:

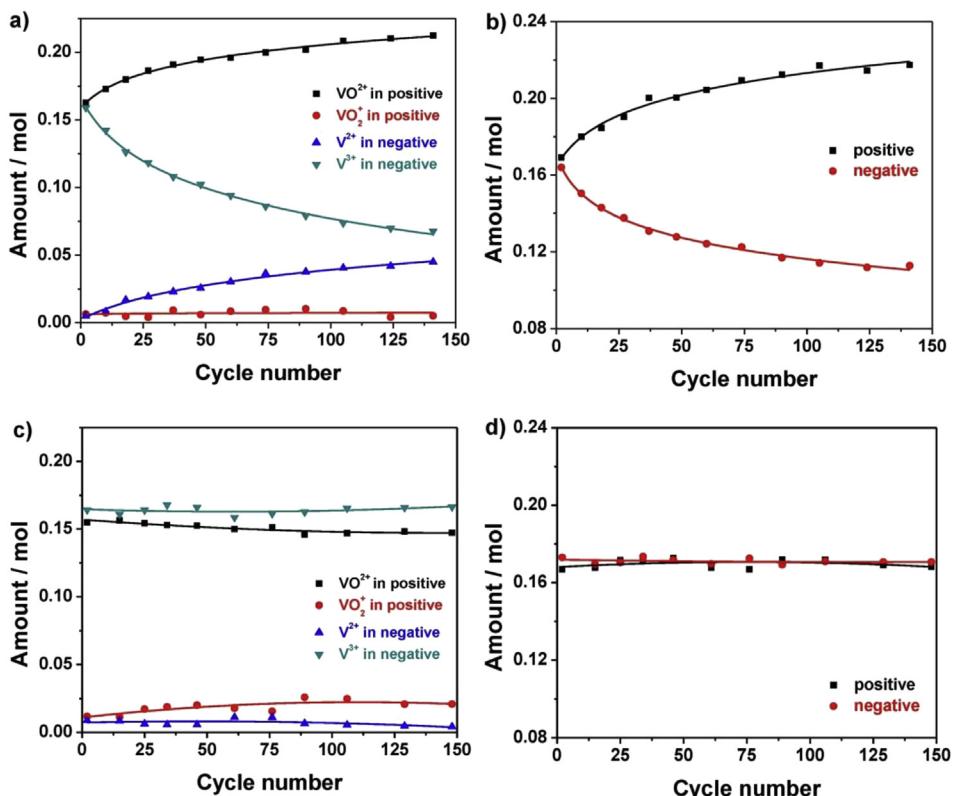
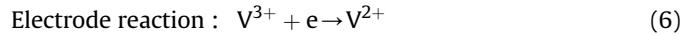


Fig. 2. Change of vanadium ions in the positive and negative electrolyte during cycle process when using Nafion 115 or VX-20 as membrane. a) Vanadium ions with different valences for Nafion 115, b) total vanadium ions for Nafion 115, c) vanadium ions with different valences for VX-20, d) total vanadium ions for VX-20.

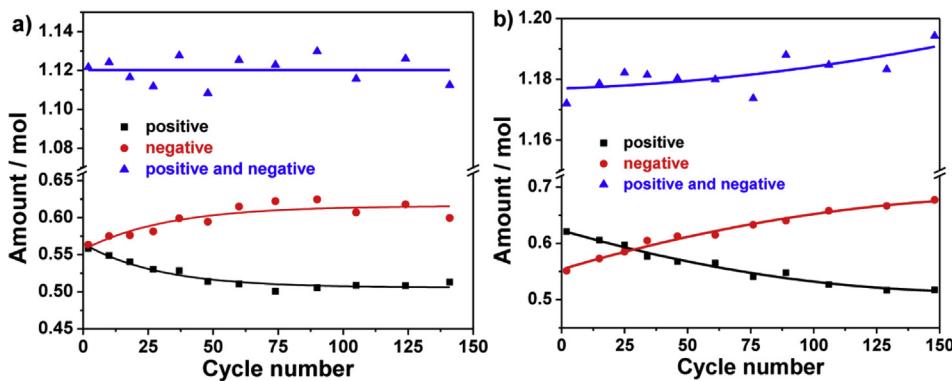


Fig. 3. Change of protons amount in the positive and negative electrolyte during cycle process when using Nafion 115 or VX-20 as membrane. a) Nafion 115, b) VX-20.

During charge process, the quantity of electrons which transmitted from positive to negative is constant, however, more electrons are consumed by side reaction at the negative side due to the fact that the side reaction on the negative electrode is faster than that on the positive electrode. [12] The electrons taking part in the negative electrode reaction decrease (as Eq. (6)), the amount of V^{2+} is lower than that of VO_2^+ during charge process as consequence. To reach the upper limit voltage of charge, more VO_2^+ will be generated at the positive side, which cannot take part in the discharge reaction and then accumulate slowly during the charge–discharge process, further leading to the decrease of VO_2^+ within a narrow range. Fig. 2d shows the amount of total vanadium ions in the positive and negative electrolyte at the end of discharge process. It can be seen that the total amount of vanadium ions is almost stable at the both sides as cycles proceeding, which is greatly different from Nafion 115. The difference is possibly caused by the functional fixed charged groups and different micro structures of the membranes. As for Nafion 115, the fixed negative charged groups can easily interact with the positive charged vanadium ions, which is beneficial for the transport of vanadium ions. While for VX-20, the fixed positive charged groups could exclude vanadium ions because of the Donnan exclusion. [17] Therefore, the permeability of vanadium ions through Nafion 115 is much higher than that through VX-20. When using Nafion 115 as membrane, the amount of vanadium ions in the positive and negative electrolyte is unbalance seriously and cannot be recovered easily due to the different hydrated states and different permeability of vanadium ions with different valences [21]. But for VX-20 membrane, the permeability of vanadium ions is rather low and the total amount of vanadium ions almost unchanged both at the positive and negative sides. Consequently, when using VX-20 as membrane, the VFB will keep very stable with cycling.

3.3. The permeability of different vanadium ions

To further confirm above assumptions, the permeability of different vanadium ions across VX-20 was detected by a diffusion cell. We found that the right cell is colorless and the concentration of vanadium ions is too low to be detected by UV–Vis spectrometer after 40 days when V^{2+} , V^{3+} or VO^{2+} was filled in the left cell. It indicated that V^{2+} , V^{3+} or VO^{2+} can hardly diffuse across the VX-20 membrane. When VO_2^+ was filled in the left cell, very low concentration of VO^{2+} (0.01087 M) can be detected in the right cell, which possibly caused by the degradation of membranes under the oxidized VO_2^+ condition. Thus, the transfer rate of vanadium ions across VX-20 is very slow and VX-20 possesses very high ions selectivity. Therefore, the permeability of vanadium ions through Nafion 115 is much higher than that of VX-20.

3.4. The transformation of protons in electrolyte

From Eqs. (4) and (6), the protons only take part in the positive reaction and they are closely related with the amount of VO_2^+ in the positive electrolyte. Once the VO_2^+ accumulates, the amount of protons will increase as well. Fig. 3 indicates the change of protons in the positive and negative electrolyte during charge–discharge process by employing Nafion 115 or VX-20 as membranes. When using Nafion 115 as membrane, the protons will permeate through the membrane to play the role of ions conduction and building a close loop with electrons: during charge process, the electrons transfer from positive to negative, meanwhile, the protons transfer from positive to negative to form the internal circuit, and the transfer direction is opposite during discharge process. During charge process, to reach the upper limit voltage of charge, more V^{2+} will be generated at the negative side during charge process owing to the highest diffusion rate of V^{2+} , thus more electrons will transfer from positive to negative side, further bring about the more transference of protons from positive to negative side. While, during discharge process, less VO_2^+ will participate in the discharge process at the positive side due to the highest diffusion coefficient of V^{2+} as well, so less electrons will transfer from negative to positive side, further leading to the less transference of protons from negative to positive side. Finally, the amount of protons descends in the positive electrolyte and ascends in the negative electrolyte after discharge process. But the total amount of protons almost unchanged. While for VX-20 membrane, the total protons increase within a narrow range during cycle process based on the Eq. (4), due to the accumulation of VO_2^+ as described above. The amount of proton increases at the negative side as show in Fig. 3b, and the protons transfer across VX-20 membrane from positive to negative side because that the protons cannot be generated or consumed in the negative according to Eq. (6).

3.5. The transformation of SO_4^{2-} in electrolyte

Apart from vanadium ions and protons, other ions like SO_4^{2-} are also presented in electrolyte. In an attempt to clarify the function of SO_4^{2-} ions during charge–discharge process, the change of SO_4^{2-} ions was investigated as well by using Nafion 115 and VX-20 as membranes. In Fig. 4, when using Nafion 115 as membrane, the amount of SO_4^{2-} increases in the positive electrolyte and decreases in the negative electrolyte, which is consistent with the transfer direction of vanadium ions. While, the transfer direction of SO_4^{2-} ions changed from positive to negative side when using VX-20 AEM, showing totally opposite tendency with that of Nafion 115 membrane.

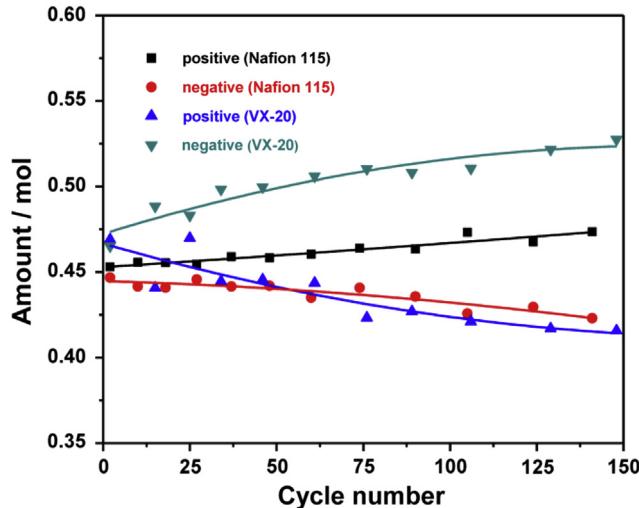


Fig. 4. Change of SO_4^{2-} amount in the positive and negative electrolyte during cycle process when using Nafion 115 or VX-20 as membrane.

3.6. The relationship of different ions in electrolyte

In summary, as for Nafion 115, the fixed negative charged groups are beneficial for the transport of vanadium ions as described above, which lead to the self-discharge reactions. But the rate of self-discharge reaction between positive and negative is different due to different permeation coefficients of vanadium ions with

different valences [21], which further lead to imbalance of vanadium ions at the both sides. The vanadium ions overall transfer from negative to positive side and the V^{2+} is accumulated at the negative side while the protons overall transfer from positive to negative side. Due to the extra positive charges induced by the transfer of vanadium ions, transference of SO_4^{2-} from negative to positive is preferred to obtain the charge balance. Therefore, the protons play the role of ion conduction and SO_4^{2-} ions play the role of charge balance in a VFB assembled with Nafion 115 as membrane. The diagram of different ions across Nafion 115 membrane shows in Fig. 5a.

VX-20 shows ultralow permeability of vanadium ions on account of the Donnan exclusion [17]. The negative charged ions can cross through the membrane due to the interaction between negative charged ions and the fixed positive charged groups in VX-20 membrane. For VX-20 membrane, the negative charge ions (SO_4^{2-}) together with protons cross through the membrane, which plays the role of ion conduction and builds the close loop with electrons. During charge process, the electrons transfer from positive to negative and SO_4^{2-} together with protons transfer from positive to negative side to form internal circuit. The amount of SO_4^{2-} transfers from positive to negative during charge process is more than that transfer from negative to positive during discharge process. Therefore the amount of SO_4^{2-} decreases at the positive side and increases at the negative side, which is opposite to that of Nafion 115. Unlike Nafion 115, the VO_2^+ accumulates in the positive electrolyte when using VX-20 as membranes, due to the different rate of side reactions at both sides as described above. With the accumulation of VO_2^+ at the positive side, the protons will accumulate within a narrow range as well. Due to the transferring of

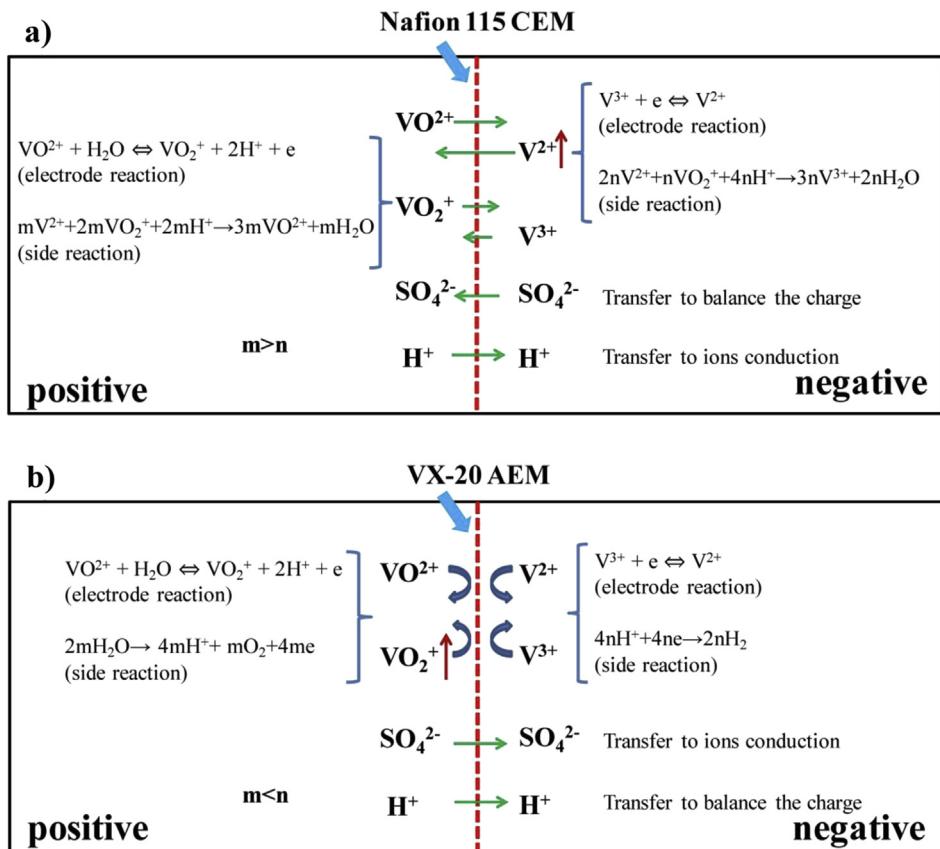


Fig. 5. Diagrams showing different ions across Nafion 115 or VX-20 membrane during the charge–discharge process. a) Nafion 115, b) VX-20.

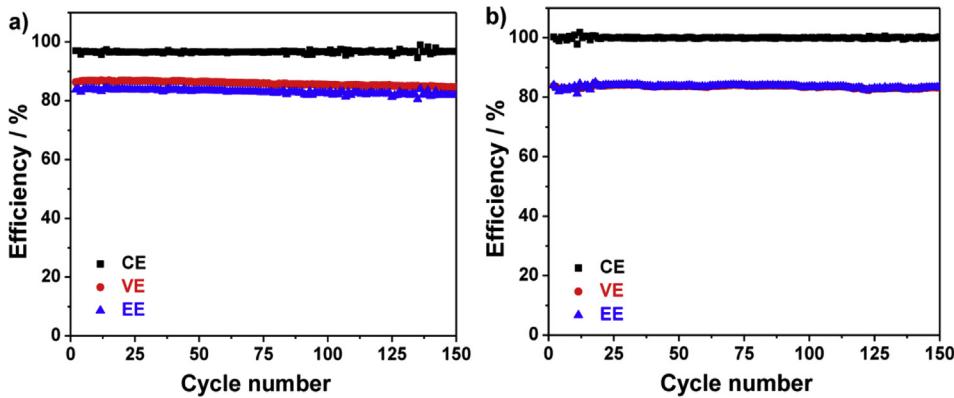


Fig. 6. The efficiency of the VFB assembled with Nafion 115 or VX-20 as membrane. a) Nafion 115, b) VX-20.

SO_4^{2-} from positive to negative side, the negative charge at the negative side increases, therefore, the transference of protons from positive balances the charge. Hence, SO_4^{2-} ions play the role of ion conduction and protons play the role of charge balance in a VFB assembled with VX-20 as membrane. The diagram of different ions across VX-20 membrane is shown in Fig. 5b. To note that this is only an overall direction, in the reality, the transfer direction could be different during charge and discharge process.

3.7. The capacity fade mechanisms

Fig. 6 shows the efficiency of VFB as cycling when using Nafion 115 or VX-20 as membrane. It can be seen that the average CE is about 96.64% and 99.99% respectively, due to the distinct selectivity between Nafion 115 and VX-20. For VX-20 membrane, the vanadium ions permeability of VX-20 is too low to be detected, the CE loss (about 0.01%) is mainly caused by the side reactions on the positive and negative electrodes. The side reactions are related to the electric potential and the set operating voltage, so no matter what kind of membranes are selected, the side reactions will occur on the electrodes, and the rate is identical once the limit voltage of charge and discharge is settled. Therefore, when using Nafion 115 as membrane, about 0.01% of CE loss will be induced by the side reactions as well. Thus it can be infer that the rest CE loss ($100\% - 96.64\% - 0.01\% = 3.35\%$) is mainly caused by the vanadium ions cross mix through Nafion 115 membrane.

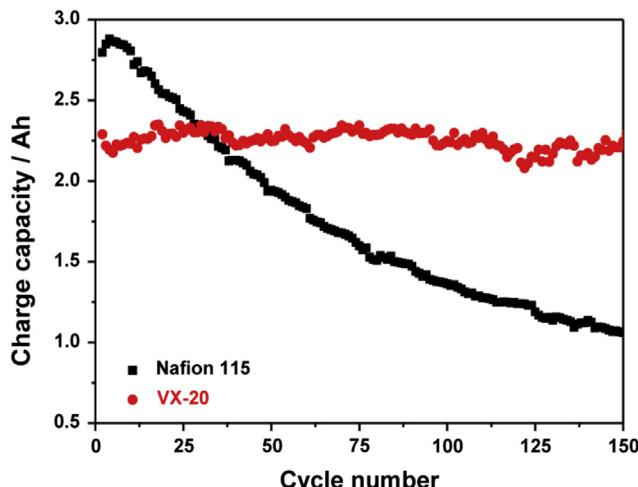


Fig. 7. The charge capacity of the VFB assembled with Nafion 115 or VX-20 as membrane.

Fig. 7 shows the charge capacity of VFB as cycling when using Nafion 115 or VX-20 as membrane, it can be seen that the charge capacity decay of VFB assembled with Nafion 115 is remarkable, while that of VX-20 is almost unchanged. The difference between them is caused by the different permeability of vanadium ions through different kinds of membranes. Due to the higher permeability of vanadium ions with different valences through Nafion 115, the vanadium ions transfer from another side could react with the active species and induce capacity decay. However for VX-20, the capacity decay is mainly derived from side reactions as described above thanks to its extremely low vanadium ions permeability.

4. Conclusions

The transfer behavior of different ions in the electrolyte across ion exchange membrane was investigated under the VFB operating condition. Nafion 115 cation exchange membrane and VX-20 anion exchange membrane were selected to survey the effect of fixed charged groups of membranes on their ions transport behavior. The accumulation and change of vanadium ions is obviously different from the anion and cation membrane due to functional fixed charged groups and different micro structures of the membranes. The V^{2+} at the negative side accumulates in the VFB assembled with Nafion 115 due to the different permeability of vanadium ions with different valences through the membrane, while the VO_2^+ at the positive side accumulates in the VFB assembled with VX-20 as membrane due to the unbalance of side reactions on the positive and negative electrodes. In addition, the interaction between different ions and water was discussed in detail: for Nafion 115, the protons play the role of ions conduction, and the SO_4^{2-} plays the role of charge balance, while, for VX-20, the SO_4^{2-} ions play the role of ions conduction and protons play the role of charge balance. Finally, the primary reasons of the capacity decay of VFB assembled with different membranes were investigated. The capacity decay rate of the VFB assembled with Nafion 115 is much higher than that of VX-20, owing to the lower ions selectivity. The capacity decay of Nafion 115 is mainly induced by the cross mix of different vanadium ions, while for VX-20, the side reactions are the main factors because of its very high resistance to the vanadium ions. These results illuminate the change of electrolyte as cycle proceeding and provide important information about electrolyte for the application of VFB.

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